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Highly stable aprotic ionic liquid doped anhydrous proton conducting polymer electrolyte membrane for high temperature applications

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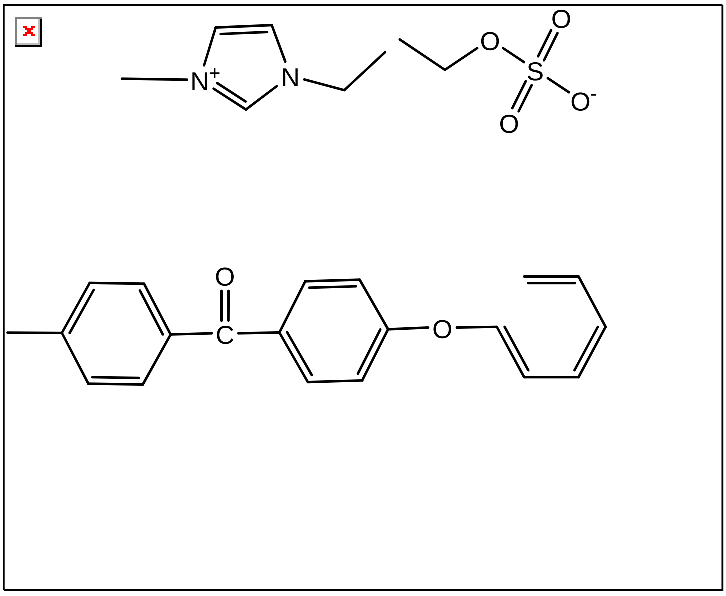
Supporting Information

Section S1. Chemical structure of 1-ethyl-3-methyl-imidazolium ethyl sulfate (EMIES) and sulfonated poly (ether ether ketone) (SPEEK)



Section S2. Procedure for the determination of ion-exchange capacity (IEC)

IEC indicates the number of miliequivalents of charge in 1.0 g of the dry polymer matrix. To determine the *IEC*, the dry membranes were first equilibrated with acid and base to ensure that all sulfonate groups converted in to sulfonic acid groups. The membranes were then washed with deionized water to remove last trace of acidity. After complete equilibration the membranes were immersed in 50 cm^3 0.1M NaCl solution for 24 h with random stirring at ambient temperature. Then 10 cm^3 of sample solution was titrated against standard NaOH solution. The sample was regenerated with 1.0M hydrochloric acid, washed to free of acid with deionized water and dried to a constant weight. The *IEC* was calculated according to the equation:

$$IEC\left(mequiv.\,g^{-1}\ dry\ membrane\right) = \frac{C_{Na^+}V_{sol}}{W_{dry}} \qquad (1)$$

Section S3. Detailed procedure for the determination of membrane conductivity at various temperatures

The membranes were sandwiched between two in-house made stainless steel circular electrodes (4 cm^2). Direct current (dc) and sinusoidal alternating currents (ac) were supplied to the respective electrodes for recording the frequency at a scanning rate of 1 μA/s within a frequency range of 10^6 to 1 Hz. The spectrum of the blank short-circuited cell was also collected and this data was subtracted (as a series circuit) from each of the recorded spectra of the membranes to eliminate cell and wiring resistances and inductances. The corrected spectra were viewed as complex impedance plots with the imaginary component of Z'' on the y-axis and the real component of Z' on the x-axis ($Z = Z'-iZ''$); the ionic resistance of each membrane was estimated to be the intersection of the x-axis with the extrapolation of the low frequency linear component of each plot. The membrane resistances were obtained from Nyquist plots by using the Fit and Simulation method.

Membrane resistance $R(\Omega)$ was measured for various membranes with various content of EMIES in the membrane matrix using the Fit and Simulation method from Nyquist plots as representative case presented in Figure 8(A) (in main text) for SPEEK and SPEEK+70wt% ionic liquid. It is evidenced that membrane resistance was decreased 10^6 times after the loading of 70 wt% ionic liquid in the membrane matrix. Proton conductivity of membrane (κ^m) was estimated by the following equation.

$$\kappa^m (S/cm) = L(cm) \big/ R(\Omega) \times A(cm^2) \qquad (2)$$

where, L is the distance between the electrodes, R is the resistance of the membrane, and A is the effective membrane area. Proton conductivity of the SPEEK and SPEEK-EMIES blend membranes were carried out on the same samples four times under anhydrous conditions, with the temperature being varied from 30 to 150 °C.

Section S4. Detailed procedure for the determination of degree of sulfonation of PEEK

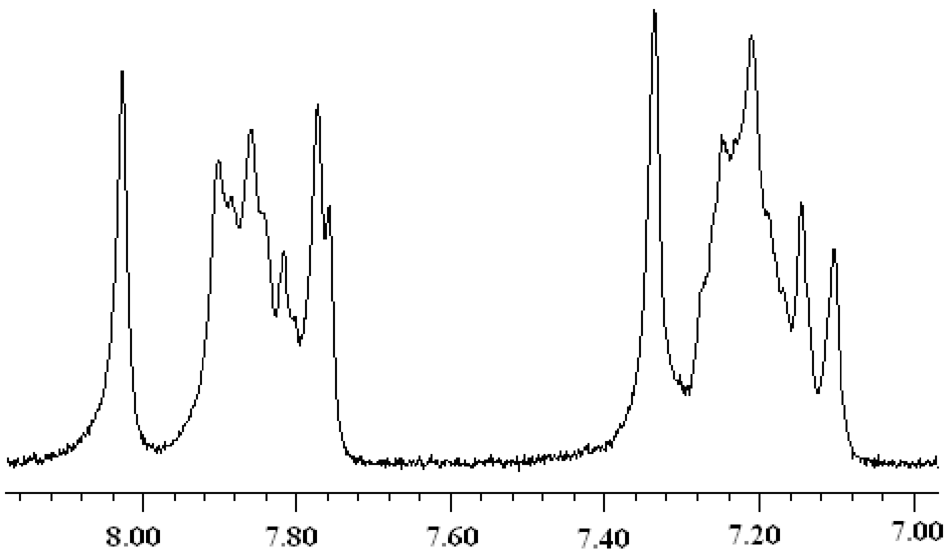
Extent of sulfonation for PEEK was estimated from ^{1}H NMR spectra presented in Fig below. Presence of a sulfonic acid group causes a significant downfield shift from 7.47 to 8.21 ppm of the hydrogen located in the ortho position at the aromatic ring. By evaluating the ratio between the peak area of the signal corresponding to the hydrogen atoms located next to the sulfonic acid groups (H_E) and the peak area of the signals corresponding to the other aromatic hydrogen atoms ($H_{A,A'B,B',C,D}$), where n is the number of H_E hydrogen atoms and 6−2*n* is the number of residual hydrogen atoms ($H_{A,A'B,B',C,D}$), degree of sulfonation of SPEEK was estimated using following mathematical expressions:

$$\frac{n}{6-2n} = \frac{AH_E}{\sum AH_{AA',BB',C,D}} \qquad (3)$$

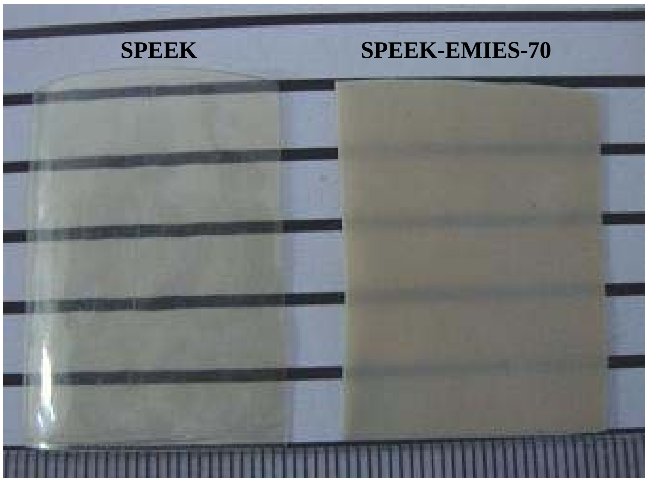
$$z = \frac{AH_E}{\sum AH_{AA',BB',C,D}} \qquad (4)$$

$$x = \frac{6z}{1/2z} \times 100 \qquad (5)$$

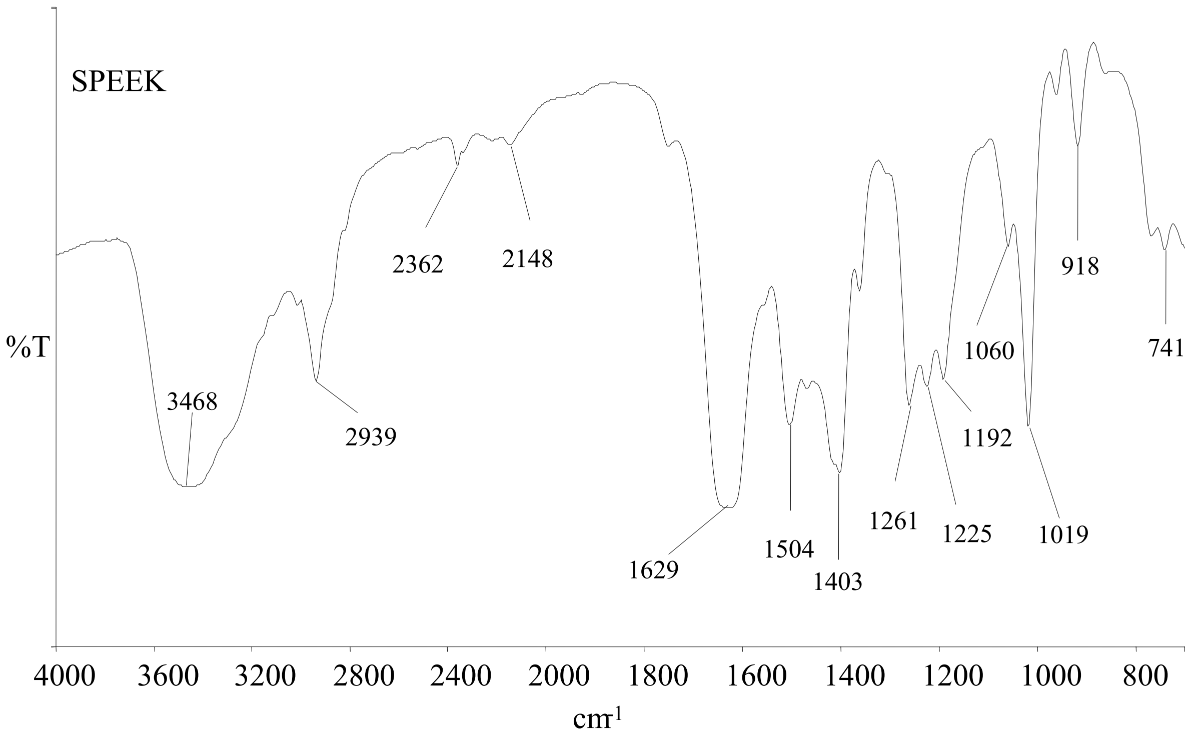
where *x* is the degree of sulfonation (mole %), AH_E is integral of H_E, $\sum H_{A,A'B,B',C,D}$ is integral of $H_{A,A'B,B',C,D}$. From Eq. (5) it was found that the degree of sulfonation for PEEK under given experimental conditions was 61.0% and it varies with time and temperature of the sulfonation.

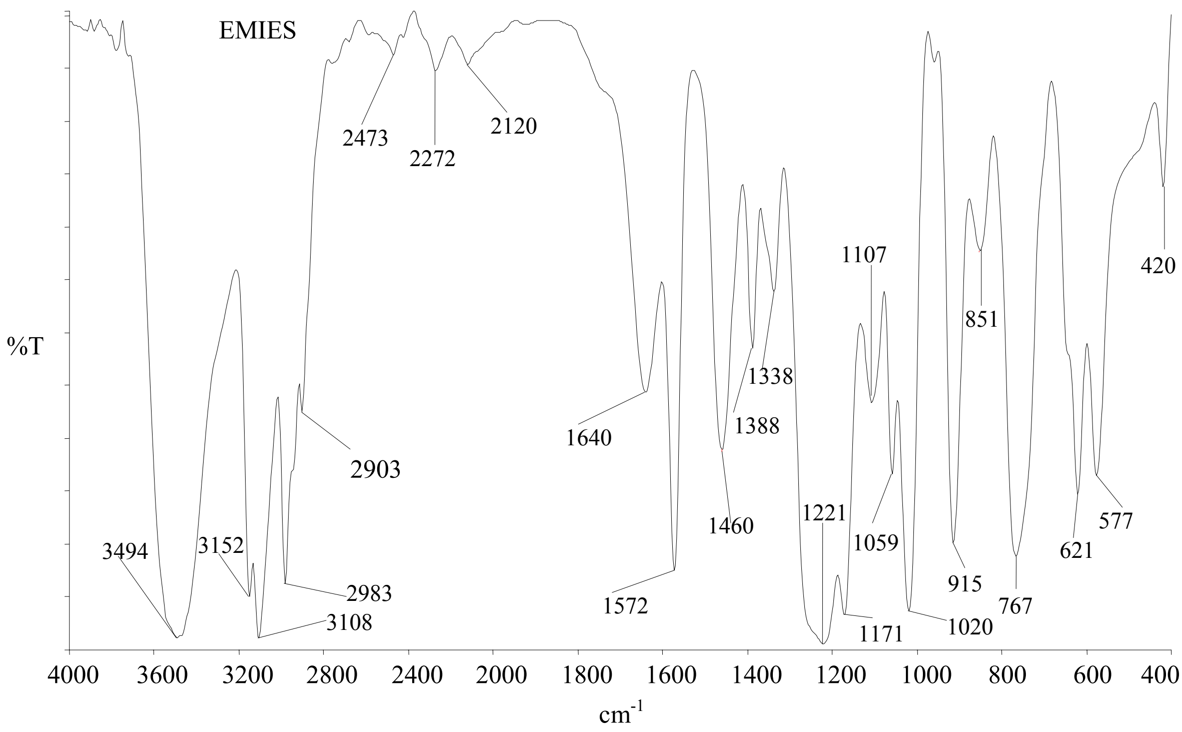


Section S5. Optical transparency of the SPEEK and SPEEK-IL-70 membranes

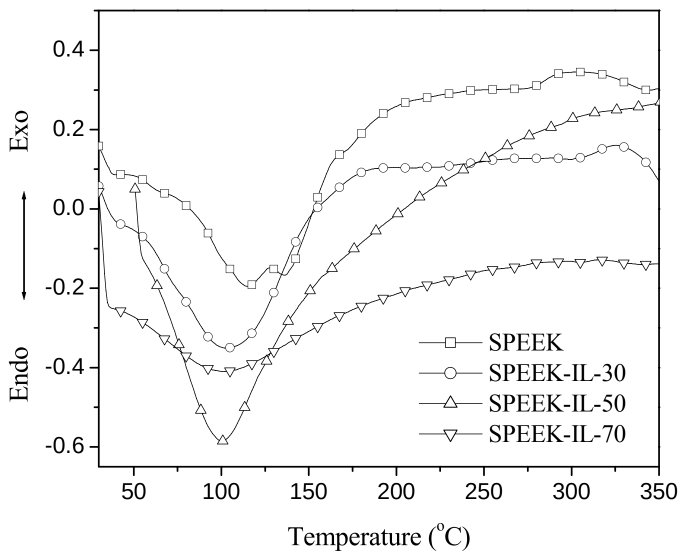


Section S6: FTIR spectra of SPEEK and IL (EMIES).

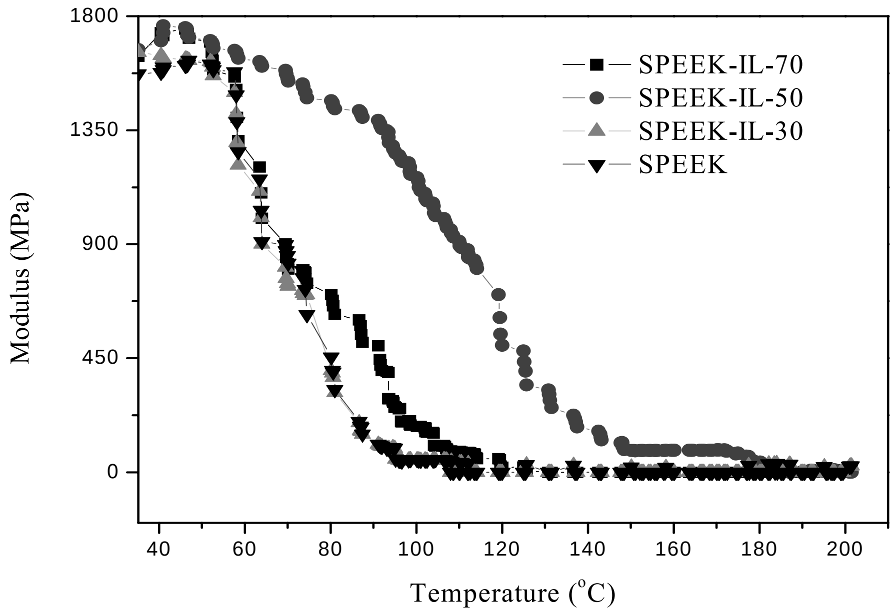




Section S7. DSC curves in fully dry state for pristine SPEEK and SPEEK-IL composite membranes with varied wt% loading.



Section S8: DMA curve for SPEEK and different SPEEK-IL composite membranes.



Section S9. Ionic conductivity of EMIES at different temperature under anhydrous condition